Electrochemical Cr-Ni-Al_2O_3 Composite Coatings Part II: Mechanical Properties and Morphology

By O. Berkh, S. Eskin and J. Zahavi

Surface morphology and some properties of Cr-Ni-Al_2O_3 electrodeposited composites, such as residual stresses, microhardness and wear resistance were investigated. Two independent methods (X-ray technique and flexible-cathode method) were applied for residual stress estimation. Al_2O_3 particles served as sensors for X-ray measurements. Dependence of the residual stresses and wear rate on particle concentration and current density was found, while microhardness was practically unaffected. The wear mechanism of the deposits is discussed in terms of residual stresses, adhesion and abrasive removal of worn material.

Highly wear-resistant coatings are required in different fields of technology, such as transportation, machine and device construction, machine tools and aircraft. Electrodeposited composite coatings on the base of a metal matrix with incorporated ceramic particles offer interesting engineering possibilities for this purpose. In view of the good wear and oxidation properties of Cr and its alloys, Cr-based composite coatings seem to be especially promising.

This paper is a sequel to the investigation reported in Part I, where the possibility of electrochemical incorporation of Al_2O_3 in Cr-Ni alloys was shown, with certain features of the suggested process permitting effective codeposition of the particles suspended in the electrolyte. In this study, some mechanical properties were examined, and an explanation of the wear behavior of the deposits was attempted.

Experimental Procedure

For Cr-Ni matrix deposition, the trivalent chromium-nickel chloride electrolyte on an N,N-dimethylformamide base was used. The coating preparation procedure was described in detail in Part I. Particle size and amount in deposits were determined by microscopic cross-section examination, as well as by EDS analysis for measuring Al concentration and calculation of the amount of Al_2O_3 in the coatings. Scanning electron microscopy (SEM) was used for examination of surface morphology. Microhardness was measured by a Vickers microhardness tester under a 25-g load. The wear behavior was examined by dry wheel abrasion tests at a rotation speed of 50 rpm under a specific load of 300 g/mm^2 on the wheel. The abrasive loss of material was determined by specimen weighing, and the linear wear rate, I, calculated according to the formula:[1]

$$I = \frac{\Delta m}{\rho \cdot f \cdot \ell}$$

where Δm is the weight loss, ρ is the material density, f is the contact area, and ℓ is the sliding distance. The complete test covered a total sliding distance of 30.8 m and was interrupted

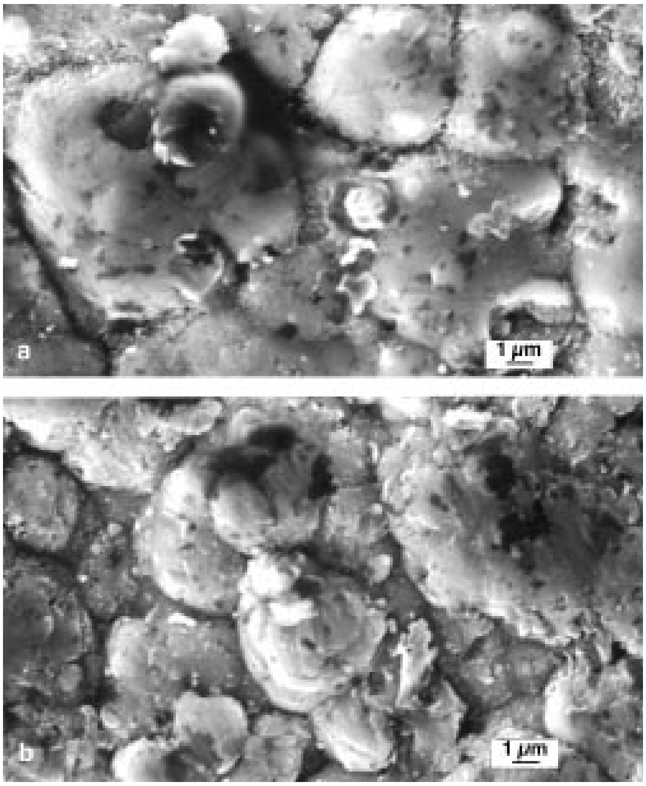

Fig. 1—Surface morphology of composite Cr-Ni-Al_2O_3 deposit. Current density, 7A/dm^2: (a) 47 and (b) 312 g/L alumina in electrolyte.

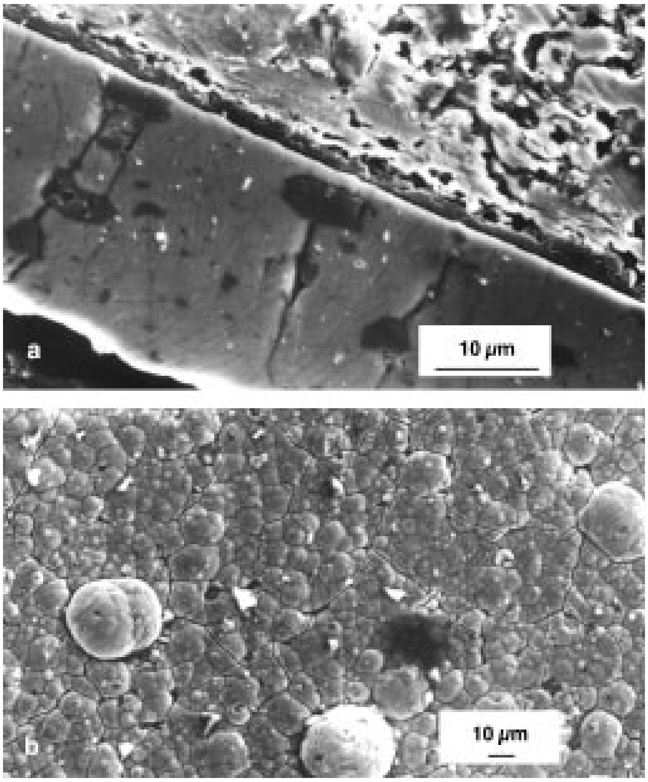

Fig. 2—Crack appearance by cross-section (a) and surface (b) examination. Current density, 21 A/dm^2; Al_2O_3 content of bath, 31 g/L.

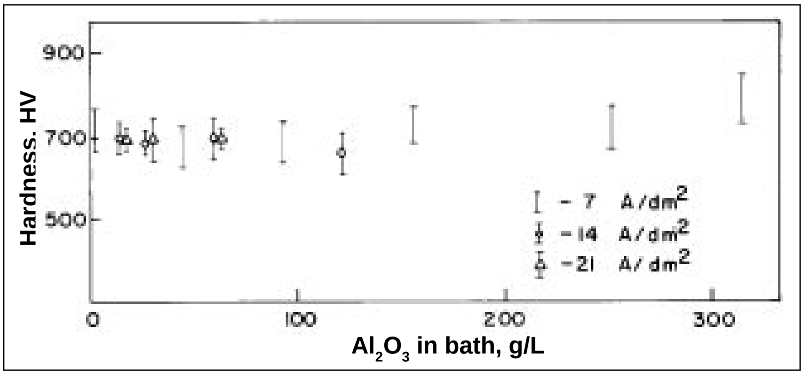

Fig. 3—Microhardness of Cr-Ni-Al_2O_3 deposit vs. alumina powder content of bath at current density 7, 14 and 21 A/dm^2.

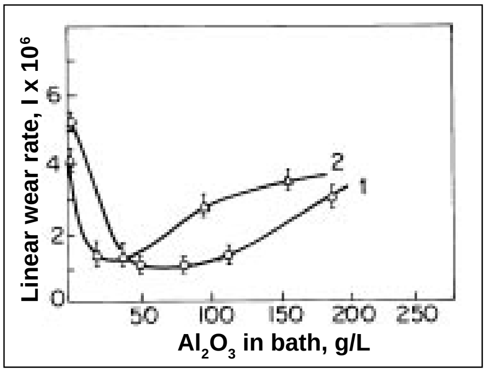

Fig. 4—Linear wear rate of composite Cr-Ni-Al_2O_3 (1) and Cr-Al_2O_3 (2) coatings as a function of Al_2O_3 content of the electrolyte. Current density 7A/dm^2.

after every 100 revolutions for weight loss measurement. The residual stresses in the coatings were determined by an X-ray technique and the flexible-cathode method,[2] using copper foil 20-µm thick. Surface roughness was examined with a profilometer. For X-ray analysis, a diffractometer was used with Cu-Kα irradiation.

Results

Surface Morphology and Roughness

Introduction of particles into the electrolytes resulted in obvious morphology changes. The originally shiny coatings became dull and their bright gray color darkened as particles were codeposited. Increase of the powder content resulted in some reduction of the average crystal size on the surface, for instance, from 8–12 µm to 3–7 µm at 47 and 312 g/L Al_2O_3, respectively, at a current density of 7 A/dm^2 (Fig. 1). Particle incorporation in an electrodeposited Cr-Ni alloy does not prevent appearance of crack networks. Cracks are seen to be through (Fig. 2a), or by-passing crystal aggregates and sometimes crossing them (Fig. 2b). The changes in morphology affected the roughness. A relatively high current density led to higher surface roughness in coatings without particles. At 14 to 17 A/dm^2, the roughness was Ra ~1.1 to 1.5, decreasing to Ra ~0.8 to 1.0 as the alumina content in the bath exceeded 20 g/L. At 7 A/dm^2 the roughness ranged from Ra ~0.8–0.9 to 0.6–0.65, as the amount of Al_2O_3 in the electrolyte increased from 47 to 312 g/L, with attendant inhibition of surface agglomeration.

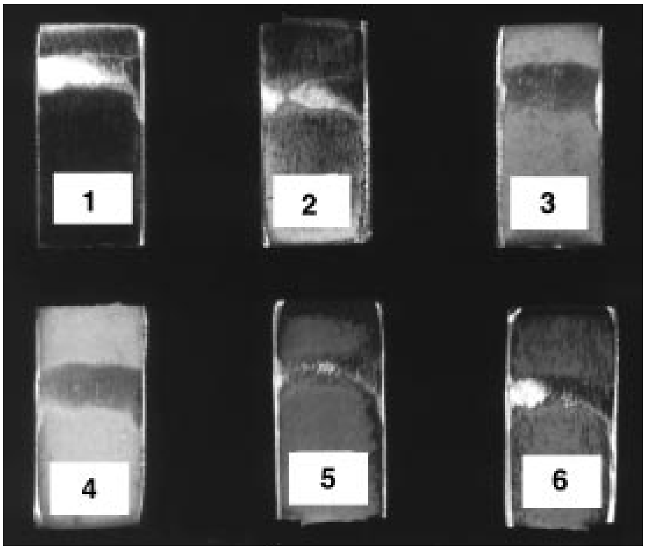

Fig. 5—Views of surfaces of worn Cr-Ni-Al_2O_3 deposits obtained at current density 7 A/dm^2; and alumina content of bath at zero (1,2), 125 (3), 50 (4), 187 (5), and 250 (6) g/L; sliding distance 26.4 (1,2) and 30.8 m (3-6).

Microhardness

Microhardness as a function of the amount of alumina in the bath is plotted in Fig. 3, which shows no increase in hardness with increasing current density and particle quantity in the bath. Average microhardness values ranged from 660 to 780 HV for alumina content of 0–312 g/L and current densities of 7 to 21 A/dm^2. The microhardness of composite Cr-Ni coatings was at the same level as that of Cr composites deposited from the same electrolyte, serving as a reference.

Wear Resistance

The wear resistance of composite Cr and Cr-Ni coatings as a function of Al_2O_3 particle concentration in the electrolyte is plotted in Fig. 4. The curve has a minimum corresponding to I ~1.1 x 10^{-6} at 15 to 45 g/L, and 45 to 110 g/L Al_2O_3 for the Cr and Cr-Ni coatings, respectively. In the absence of particles, or at excessive particle amounts, the wear rate was three to five times the minimum, and the resultant heavy or total damage is seen in Fig. 5.

A moderate amount of alumina in the bath, corresponding to 1–1.5 wt percent of Al_2O_3 in the coating, produced uniform removal of the deposit. Microscopic examination of the worn surfaces showed grooves in the wear track, co-directional with the movement of the wheel. At powder contents above 80–90 g/L, and especially above 130–150 g/L, flaking was observed against the background of the abrasion scratches (Fig. 6). Intensified wear was also observed as current density increased (Fig. 7).

Residual Stress

The X-ray diffraction spectra indicated an amorphous structure for the composite coatings. Accurate stress analysis based on peak shifts and shape changes were impossible in the absence of a pronounced maximum in the Cr-line; therefore, corundum peaks were used as a reference for measurements. Matrix strains were evaluated on the assumption of all-around strain isotropy and equal transmission of the load to the particles and matrix. By measuring the lattice constants a and c of hexagonal corundum, the strains (for instance, in the z-direction) can be defined as $\varepsilon_z = \Delta c/c$, where Δc is the decrement of c.

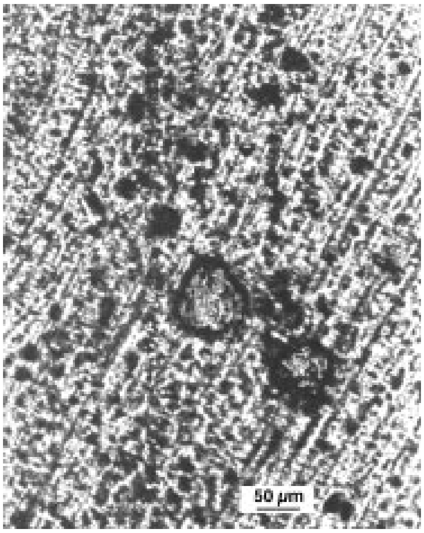

Fig. 6—Worn specimen surface after sliding distance of 30.8 m. Current density, 7 A/dm^2, Al_2O_3 in bath, 187 g/L.

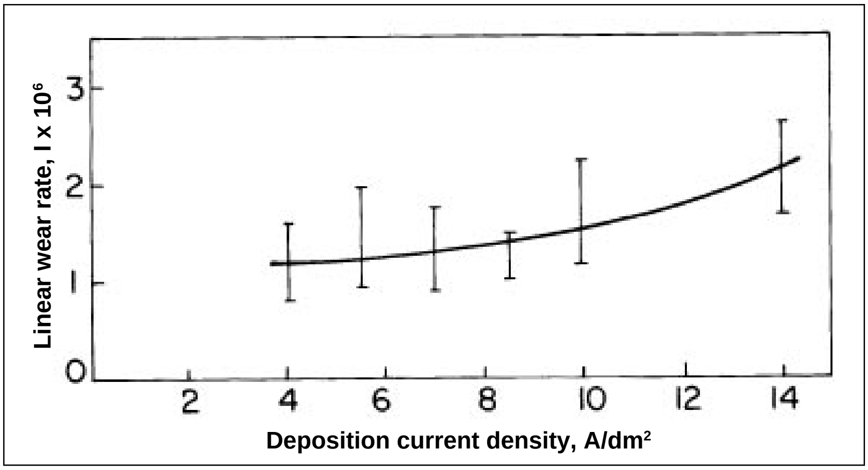

Fig. 7—Effect of current density on linear wear rate of Cr-Ni-Al_2O_3 deposits with 75 g/L alumina powder in the electrolyte.

Further evaluation of the residual stresses is possible on the basis of two-dimensional or three-dimensional analysis. The average depth of X-ray penetration with Cu-Kα irradiation is estimated at 5 to 7 μm, which, considering the observed preferential codeposition of fine particles 1–2 μm in size at rather high powder amounts in the bath, is at least three to five times the average particle size. Consequently, in the surface layer of X-ray penetration, the particle is probably surrounded by the matrix material and the three-dimensional stress-field model is more justified. The matrix and particle stresses can be calculated via the well-known stress-strain relationships,[3] namely,

$$\varepsilon \equiv \Delta c/c = \sigma^p/E^p(1-2\upsilon^p) = \sigma^m/E^m(1-2\upsilon^m) \qquad (1)$$

resulting in

$$\sigma^m = \Delta c/c(E^m/1-2\upsilon^m) \qquad (2)$$
$$\sigma^p = \Delta c/c(E^p/1-2\upsilon^p) \qquad (3)$$

where E^m, υ^m, E^p and υ^p are Young's modulus and Poisson's ratio for the matrix and particle materials, respectively, and σ^m and σ^p are the matrix and particle stresses.

For the coatings obtained with 90-percent Cr and 10-percent Ni, $\upsilon^m = 0.285$ and $E^m = 246$ GPa was acceptable.[4] The c- and a-parameters of α-Al_2O_3 crystals were determined through measurement of the lattice interatomic spacing, where good precision (~1×10^{-4}) was obtained.

Figure 8 shows the effect of the amount of powder in the electrolyte and of the current density on the residual stresses. As expected, they were of tensile character and ranged from 0.1 to 1.2 GPa. Calculation of the residual stresses for the coatings deposited at 7 A/dm^2 with Al_2O_3 content of 47 and 128 g/L, using the a-parameter, yielded stress values of 0.34 and 0.14 GPa, respectively.

Macrostress estimation by the flexible-cathode method showed a similar trend of stress variation with current density and quantity of powder in the electrolyte, but the typical values of the tensile stresses (*e.g.*, 0.06 GPa at 7 A/dm^2 and Al_2O_3 content 45 g/L) were almost 20 and five times lower than those obtained via the c- and a-parameters, respectively.

The approach based on X-ray analysis did not cover the stresses close to the matrix/particle interface; thus, the strains in the matrix and Al_2O_3 phase were accepted as equal, while stresses differed only because of different values of the mechanical constants. The alternative approach allows for microstresses close to the matrix/particle interface and the particle amount in the deposit. The matrix stresses can then be evaluated from the equation[5]

$$\sigma^m v^m + \sigma^p v^p = 0 \qquad (4)$$

where v^m and v^p are the volume portions of matrix and particles, respectively. At $E^{Al_2O_3} = 380$ GPa and $\upsilon^{Al_2O_3} = 0.27$,[6] the calculation by Eqs. (3) and (4), via the c-parameter, yields residual stress values of 0.03 and 0.02 GPa, respectively, at 47 and 128 g/L of alumina in the electrolyte. Accordingly Eq. (4) yields better agreement, compared with the flexible-cathode technique, exhibiting only a two-fold difference in stress values.

Discussion

The results showed that particle incorporation noticeably influences the morphology, residual stresses and wear resistance of Cr-Ni alloys, while microhardness remains invariant. Improved wear performance, as a result of hard particle incorporation, was observed earlier for Cr-coatings deposited from a conventional electrolyte.[7-9] The optimum particle content was indicated by Young,[7] as well as in this study.

The invariant character of the microhardness conflicts with some of the data, which showed that microhardness more often increased[10-12] or decreased[7] as a result of particle incorporation. Our own and cited results do not indicate a direct relationship between microhardness, on the one hand, and the size of the particles used and the uniformity of their distribution in the coating, on the other. Although these factors are certainly relevant, the foremost factor appears to be the matrix structure, as affected by the codeposited particles. The results obtained did not indicate considerable structural transformation of the Cr-Ni alloy matrix. Reduction of the residual stresses resulting from particle incorporation could be attributed to impeded dislocation movement[13] and supported by analogous results characteristic of Ni deposits with TiC, WC and ZrO_2 particles.[14]

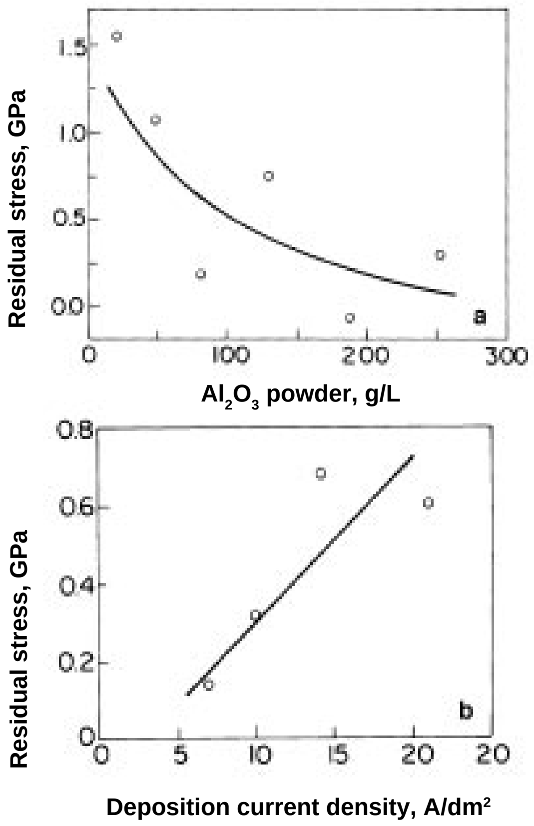

Fig. 8—Effect of current density (a) and amount of alumina powder in bath (b) on residual stresses in Cr-Ni-Al_2O_3 deposits: (a) Al_2O_3 in bath 75 g/L; (b) current density, 7 A/dm^2.

The difference in residual stress values when measuring the c- or a-parameter of the Al_2O_3 crystal is associated with the anisotropic elastic properties of corundum. Good agreement of the results obtained by the flexible-cathode and X-ray techniques, using Eq. (4), confirmed the presence of microstresses near the particle/matrix interface.

Typical scratches on the specimen surface indicate abrasive removal of coating material. Increase of powder content in the bath, and consequently in the deposit, caused marked wear rate reduction. Also, powder increase in the electrolyte increases the tendency for preferential trapping of fine particles that can improve the wear resistance.[15] As shown by Hu,[8] the wear resistance of Cr-SiC composites was also higher as finer particles were incorporated in the deposit. The enhanced wear at excessive particle concentration can be ascribed to another mechanism, namely, reduction of the adhesive and cohesive forces. Poor adhesion led to brittle flaking of the less-adhesive coated regions. Enhanced coating removal at low alumina amounts and high current densities could be attributed also to fatigue destruction, which is especially sensitive to tensile stresses in the surface layer. This effect, however, cannot be dominant in view of the monotonic decrease of the residual stresses with increasing Al_2O_3 (Fig. 8b), while the wear resistance plot (Fig. 4) shows a distinct minimum.

Conclusions

Al_2O_3 particle codeposition with a Cr-Ni alloy matrix resulted in reduction of surface roughness, residual stresses and wear resistance. The composite Cr-Ni coatings obtained, however, exhibited remarkable cracking, like deposits without particles. The linear wear rate of the deposits was characterized by a minimum at 45 to 110 g/L Al_2O_3 in the electrolyte, despite the fact that microhardness remained unaffected (at about HV 700) with various amounts of particles. Reduction of the wear resistance at very high alumina content is mainly attributed to poor adhesion and spalling of the less-adhesive coated regions.

X-ray technique permits residual-stress analysis using alumina particles as a reference. Evaluation of the residual stresses in such deposits should be conducted with allowance for the microstresses resulting from interphase matrix and particles interaction.

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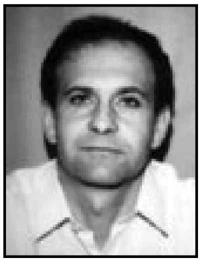

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